ANNUAL CONFERENCE ON FIRE RESEARCH
Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

Building and Fire Research Laboratory
Gaithersburg, Maryland 20899

ANNUAL CONFERENCE ON FIRE RESEARCH
Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

FLAMMABILITY OF CYANATE ESTER RESINS

*R.N. Walters *, S. Gandhi * and R.E. Lyon*
Fire Safety Section AAR-422
Federal Aviation Administration
W.J. Hughes Technical Center
Atlantic City International Airport, NJ 08405

* *Galaxy Scientific Corporation*
Egg Harbor Township, NJ 08234

Cyanate ester resins are being considered for composite applications in commercial and military aircraft because of their good thermal and mechanical properties and ease of processing. The cyanate ester resins are a one part system where several reactive -OCN functional groups undergo a cyclotrimerization reaction to form a six membered triazine linkage [1] as shown in figure 1. When multifunctional cyanate ester monomers react, the triazine ring formation serves as the polymerization reaction forming a highly crosslinked structure. There are no catalysts, curing agents or additives needed for the curing process and no by-products or voids are formed in the matrix [2]. Previous studies have show the glass transition temperature increases with increasing functionality of the monomer from about 200°C for difunctional monomers to above 400°C for trifunctional monomers [3]. The flammability of the series of polymers with varying crosslink densities due to their backbone structure and functionality will be presented.
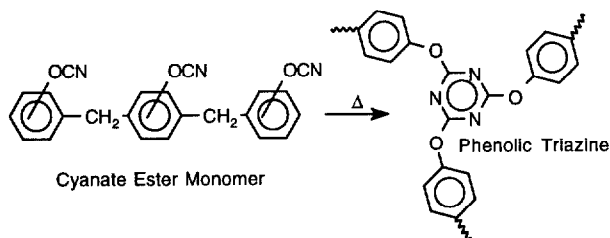

Figure 1: Cyclotrimerization reaction of the cyanate ester novolac to form the cyanurate network.

The resin samples for these experiments were used as received without any additives or purification. Cyanate esters B-10, F-10, L-10, M-10, XU-366 and XU-371 were from Ciba Specialty Chemicals and PT-30, PT-60 and PT-90 were from Allied-Signal Corporation. Table 1 shows the trade names and monomer structures of the materials. Samples were required for bomb calorimetry, thermogravimetric analysis (TGA), fire (cone) calorimetry, as well as for pyrolysis-combustion flow calorimetry (PCFC). All of the samples were cured by gradually heating the degassed resin in steps until the samples were solid then followed by a higher temperature post-cure.

Weight loss data was taken on a commercial thermal gravimetric analyzer (Perkin Elmer TGA 7). Samples weighing from 5 to 10 mg were heated from 50-1000°C at 10°C/min under nitrogen. From the experiments the onset of degradation, peak mass loss rate and char yield are determined.

Values for the gross heat of combustion were obtained with an oxygen bomb calorimeter (Parr Instrument Model 1341) using ASTM method D 2382-88 [4]. Samples of approximately 1 g each were run in triplicate to provide both the gross and net heats of combustion.

Table 1: Trade names and monomer structures of the cyanate ester resins.

Bench scale heat release rate data was obtained using a cone calorimeter (CONE2, Atlas Electric Devices) according to ASTM E-1354 [5] at radiant heat flux levels of 35, 50, 75 and 100 kW/m^2. Sample plaques for the test weigh around 75 g and measure 10 x 10 x 0.64 cm. Single samples of each cyanate ester were tested at each heat flux level in the horizontal configuration with an edge frame. Properties determined are the heat release rate from oxygen consumption, mass loss rate, smoke production, CO and CO_2 production, time to ignition and effective heat of combustion. From a series of tests at different heat flux

levels properties such as the heat of gasification and critical heat flux for ignition were also determined.

Microscale heat release data was obtained for the cyanate esters using a pyrolysis-combustion flow calorimeter developed by the FAA [6]. Approximately 1 mg of sample is pyrolyzed at 5°C/s in a nitrogen environment to simulate non-oxidative pyrolysis at the sample surface in a diffusion flame. The decomposition products are then completely oxidized in a high temperature combustion furnace. The combustion products are removed from the gas stream and the oxygen concentration measured over time. The heat release rates are obtained by using the oxygen consumption principle with Thornton's rule [7,8]. The properties that are determined are the peak heat release rate in W/g, heat release capacity in J/g-K, total heat released in kJ/g and the char yield in percent.

TGA shows the 5 % mass loss for all of the materials falls between 436 and 457°C which suggests a similar mechanism involving the triazine linkage which is independent of the backbone structure. The heat of complete combustion determined by bomb calorimetry is similar for all of the cyanate esters tested except for the fluorinated F-10 resin.

Fire calorimeter data show the shape of the heat release rate curves are highly dependent on the backbone structure of the cyanate ester. The burning behavior exhibited by the materials is related to the crosslink density, which is known to effect the fracture toughness and tear resistance of crosslinked materials in the leathery state. In general, the fire behavior can be described as ignition of the surface with rapid charring followed by surface cracking, the development of porosity and,/or swelling of the charring sample. Also, aromatic content, and gas permeability of the char appear to influence the fire response of thick specimens. A large crack which releases a burst of trapped volatiles gives rise to the high secondary heat release peak as for PT-30/60/90 and XU-371. The high crosslink density of phenolic triazines tends to cause the formation of thicker char. Large cracks which formed during burning of the series of cyanates indicate their brittle behavior. Distributed small cracks and porosity in the degrading and charring bisphenol cyanates L-10, B-10 and M-10 produce the diffuse secondary heat release peaks. The XU-366 and XU-717 exhibit very broad secondary heat release rate peaks which is associated with a large increase in the sample thickness due to the material intumescing. Figure 2 shows the trend in heat release rate at a 50 kW/m² heat flux for all of the cyanates tested. Data for 35, 75 and 100 kW/m² will also be presented.

Microscale PCFC data does not appear to correlate wholly with the bench scale fire calorimeter data. Surface effects and thermal diffusivity associated with the geometry and sample orientation are present in the bench scale test that are not in the microscale test.
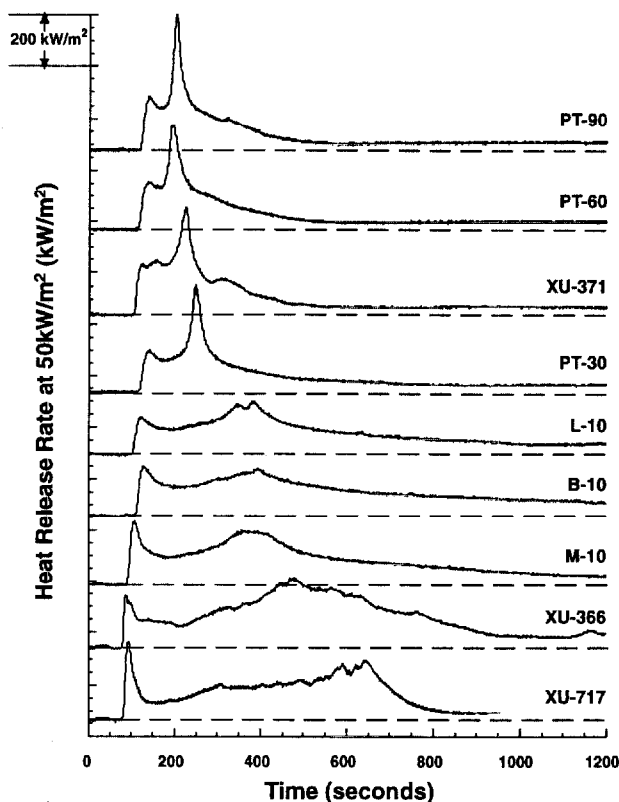

Figure 2: Heat release rate curves for the cyanate esters at 50 kW/m²

All of the data mentioned will be presented and trends in the data relating to the structure will be discussed.

REFERENCES

1. Grigat, E.; Putter, R. *Angew. Chem. Internat. Edit.*, 6, 3, 207, **1967**.
2. Das, S.; Prevorsek, D. C.; DeBona, B. T., *Mod. Plast.*, Feb. **1990**.
3. I. Hamerton, Chemistry and Technology of Cyanate Ester Resins, Blackie Academic and Professional, London **1994**.
4. ASTM Fire Test Standards, 3rd Edition, D2382-88," Standard Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High Precision Method)," pp. 230-238, American Society for Testing of Materials, Philadelphia, PA, **1990**.
5. ASTM Fire Test Standards, 3rd Edition, E1354-90,"Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter," pp. 803-820, American Society for Testing of Materials, Philadelphia, PA, **1990**.
6. R.N. Walters and R.E. Lyon ,"A Microscale Combustion Calorimeter for Determining Flammability Parameters of Materials," Proc. 42nd Int'l SAMPE Symposium and Exhibition, 42(2), 1335-1344, **1997**.
7. W.M. Thornton, *Philos. Mag.* 33, 196, **1917**.
8. Clayton Hugget, Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements, Center for Fire Research, National Bureau of Standards, Washington, DC 20234, *Fire and Materials* Vol. 4 (2) **1980**.